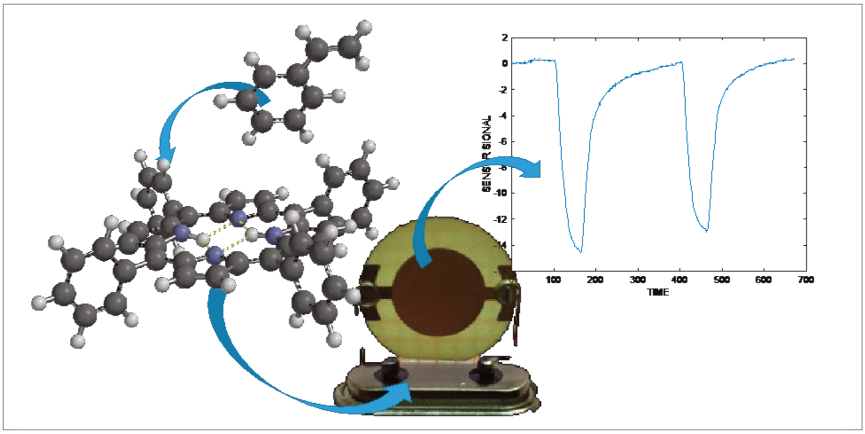
Sensor systems for volatile compounds and micro-organisms in working sites



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Giancarlo Della Ventura - Corrado Di Natale - Antonella Macagnano

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Cover page: schematic assemblage of a sensor for VOCs based on porphyrinoids nanolayers on a quartz microbalances.

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Authors*:

Ilaria Amori, Lorenzo Avaldi, Joshua Avossa, Catia Balducci, Andrea Bearzotti, Carlo Callegari, Alessandro Capocecera, Rosamaria Capuano, Alexandro Catini, Angelo Cecinato, Alessandra Chiominto, Marcello Coreno, Annalisa, D'Arco, Fabrizio De Cesare, Giancarlo Della Ventura, Marta Di Fabrizio, Corrado Di Natale, Valerio Dolci, Massimiliano Frattoni, Andrea Gordiani, Ettore Guerriero, Sergio Iavicoli, Plinio Innocenzi, Nunziata L'Episcopo, Stefano Lupi, Antonella Macagnano, Ludovica Malaguti Aliberti, Luca Malfatti, Antonella Mansi, Augusto Marcelli, Anna Maria Marcelloni, Stefano Orlando, Emilia Paba, Roberto Paolesse, Paolo Papa, Mattia Perilli, Massimo Petrarca, Susanna Piccirillo, Anna Rita Proietto, Francesco Radica, Giuseppe Scarascia-Mugnozza, Paola Tomao, Giovanna Tranfo, Emiliano Zampetti, Eyal Zussman.

*These authors presented the scientific reports collected in this book at the final meeting on the results of the BRIC2016-ID12 project, held in Rome, Italy, October 25, 2019.

Papers presented at the final meeting on the results of the BRIC2016-ID12 project financed by INAIL:

Progettazione e sviluppo di un sistema sensoriale per la misura di composti volatili e l'identificazione di microorganismi di interesse occupazionale.

Rome, Italy, October 25, 2019

Organized by:
University of Roma Tre,
University of Rome Tor Vergata,
CNR - Institute of Atmospheric Pollution,
INAIL-DiMEILA

Scientific Committee
Giancarlo Della Ventura (University Roma Tre)
Augusto Marcelli (INFN)
Corrado Di Natale (University Tor Vergata)
Antonella Macagnano (CNR-IIA)
Giovanna Tranfo (INAIL-DiMEILA)
Andrea Militello (INAIL-DiMEILA)
Emilia Paba (INAIL-DiMEILA)
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Sergio Iavicoli (INAIL-DiMEILA)
Emiliano Zampetti (CNR-IIA)
Rosamaria Capuano (University Tor Vergata)

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Preface

Sergio Iavicoli, *Director of the Department of Occupational and Environmental Medicine, Epidemiology and Hygiene - INAIL*

This book collects the contributions presented at the workshop dedicated to the presentation of the results of the project BRIC 2016 – DiMEILa ID 12 "Design and Development of a Sensory System for the Measurement of Volatile Compounds and the Identification of Microorganisms of Occupational Interest", held on October 25th in Rome. The project is supported by INAIL (the Italian workers' compensation Authority) in the framework of the collaborative research bids which the Institute publishes annually (Bric) to achieve the planned research objectives and to enhance its scientific network of excellence.

The present project has been aimed at addressing a problem of paramount importance for workers safety, i.e. the set-up of portable and possibly personal instruments for the monitoring of hazardous volatile organic compounds (VOCs) in working sites.

Current validated methods for measuring exposure to airborne chemical agents use static samplers and analytical techniques that provide an off-line and time-averaged response; using these methods to capture space-time heterogeneity and identify pollution peaks would be prohibitively expensive. The existing direct reading instruments hardly meet the necessary requirements for the evaluation and prevention of exposure to dangerous chemical agents in workplaces.

For this reason it has been considered as a priority of the Authority the development of specific, robust and reliable chemical sensors able to provide identification and real time measurements allowing, besides information on space-time distribution of chemical pollution, a rapid decision-making process in case of danger.

This challenge has been faced thanks to a collaboration between the University of Tor Vergata (Dept. of Electronic Engineering), University of Roma Tre (Dept. of Science) and CNR (Dept. of Atmospheric Pollution Research), in strong synergy with INAIL-DiMEILA. The objective of this project has been the design of new instruments, based on innovative technologies, able to provide a response as sensitive, specific and quantitative as possible, for VOCs considered as hazardous by the current regulation, as well as for volatile substances generated by bacteria and fungi. The three different groups studied different strategies, involving different methods to capture and measure the target substances. The different methods were finally combined and tested as an integrated system that is still under development. This integrated system could represent a new tool for real-time monitoring that the workers' exposure remains at acceptable levels, and for improved prevention of occupational diseases due to chemical and biological agents.

Introduction

Corrado Di Natale, *University of Rome Tor Vergata*
Antonella Macagnano, *CNR-IIA*
Giancarlo Della Ventura, *University of Roma Tre*

With the term VOCs we intend the volatile portion of those compounds that in normal conditions have not undergone a phase transition. Volatile compounds (VOCs) basically occur in all natural and artificial processes. In working sites, sources of VOCs are countless; they include all chemical families and have a different impact on human health.

Additional sources of VOCs are the metabolic processes in living beings, including the VOCs released by humans and animals and also those produced by microorganisms such as bacteria and fungi. All of these reasons make the VOCs analysis a crucial element of environmental monitoring.

Considering the ubiquities and the vastity of VOCs, it is immediately apparent that this project has addressed a very ambitious goal because the development of specific sensors, each effective for each VOC, can be considered as a rather unrealistic target.

For these reasons the project has been oriented towards the implementation of the principle of combinatorial selectivity used by Nature for the sense of olfaction. The basic idea of this principle is that an array of broadly selective sensors can encode the composition of gaseous samples into multidimensional signals, and the multivariate analysis of these signals provides the identification of the main characteristics of the sample. Furthermore, these arrays are optimal in determining the variation of compositions, thus evidencing any deviation from normal behavior.

Combinatorial selectivity requires that the sensitivity and selectivity of sensors should be more different as possible. Thus, the project considered different sensing materials and transducers technologies. Interesting results have been obtained with sensitive materials made of solid state layers of porphyrins, of hybrid materials made of porphyrins grafted onto zinc oxide nanoparticle, of electrospun fibers of cocktails of polymers, graphene and porphyrins, and finally of mesoporous silicon thin films. Transducer techniques involved quartz microbalance and impedance measurements. Specific electronic units have been designed and tested, they resulted in portable instruments that could be used for tests on fields. Additional results included the study of FTIR spectroscopy for the detection of gaseous substances and the design of an original purge and trap device. Sensors have been tested for a number of compounds, for instance quartz microbalance sensors shown sufficient sensitivity to detect styrene below the threshold concentration in working place, and QMB based sensor array were tested to detect microorganisms in the environment. Tests of using THz spectroscopy, a technique very poorly explored for the analysis and identification of the different volatile compounds, have also provided very interesting results and have shown how this spectral region has very promising potential as an analytical tool for environmental monitoring.

A selection of the results obtained during these two years are presented at the workshop and are included in this booklet.

Besides the scientific results of the project, we intended to enrich the workshop with additional presentations aimed at clarifying those regulatory aspects that are often poorly known to the community more specifically focused at the technical aspects. For this reason, we invited a talk, given by Dr. Ludovica Malaguti, focused on the subject of legislation about VOCs in working places. Two final talks intend to rise the attention towards novel technologies for VOCs detection and sensor materials development and characterization. These talks will discuss the sensing properties of electromagnetic radiation in the bands of THz and extreme ultraviolet with synchrotron sources.

We believe that the project has been particularly productive and we do hope that the obtained results and the acquired knowledge may be useful for the progresses in this field. We like to emphasize that these results have been obtained thanks to the continuous and fruitful collaboration with the staff at INAIL-DiMEILA, in particular we are in debt with Dr. Giovanna Tranfo, Dr. Antonella Mansi and Dr. Emilia Paba for their competent and active support.

Occupational Exposure Levels in the European legal framework on Occupational Safety and Health at workplace

Ludovica Malaguti Aliberti*

**Presidente "Comitato Consultivo per l'Aggiornamento Valori Limite di esposizione professionale" presso Ministero Lavoro e Politiche Sociali*

*corresponding author: Ludovica Malaguti Aliberti
Email: *ludovica.malaguti@iss.it*

Key words: chemicals, risks at workplaces, Occupational limit Values

In line with the Treaty on the Functioning of the European Union (TFEU), the EU and the Member States are intended to have, as one of their objectives, the promotion of improved working conditions. To achieve this objective, the EU shall support and complement the Member States in improving the working environment to protect workers' health and safety.

The legal European framework on Occupational and Safety Health (OSH) is aimed at protecting workers safety in the workplace. It requires employers to carry out a workplace risk assessment of all safety and health risks, including those from dangerous substances, and to set appropriate protection and prevention measures. The relevant EU legislation to protect from exposure to dangerous substances are the Chemical Agents Directive (CAD), the Carcinogens Directive (CMD), and the directives on limit exposure values.

The first priority is to ensure that risks are kept under control and is tackled at the source by making collective measures that protect in a systematic way.

Similarly the European legislation on chemicals products REACH (Reg. 1907/2006/UE) and CLP (Reg. 1272/2008/UE) are adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals, while enhancing the competitiveness of the EU chemicals industry. It also promotes alternative methods for the hazard assessment of substances in order to reduce the number of tests on animals.

Regulations require chemical manufacturers and suppliers to ensure that standardized safety labels, hazard pictograms and safety data sheets are provided. These provide information on the properties of substances and the hazards associated with them, and guidance on storage, handling and risk prevention. Furthermore guidelines and some other specific legislation cover specific aspects, such as manufacturing, supplying, transporting and labeling dangerous substances, and these are often relevant to the workplace too.

The Scientific Committee on Occupational Exposure Limits for Chemical Agents (SCOEL) was set up by Commission Decision 95/320. Its purpose is to evaluate the health effects of chemical agents on workers and to provide the Commission with opinions relating to the toxicological examination of chemical agents. It ensures that Commission proposals, decisions and policy relating to the protection of workers' health and safety are based on sound scientific evidence.

In the 90s it was introduced into EU legislation the objective of establishing OELs (Occupational Exposure Levels) for chemical agents that workers are exposed to. This was accomplished through implementation of the Directive 98/24/EC on chemical agents (the Chemical Agents Directive CAD) and the Directive 2004/37/EC on carcinogens or mutagens (the Carcinogens and Mutagens Directive CMD). In fulfilling this objective, since 1998, SCOEL established OELs on the basis of advice from expert independent. The establishment of OELs is complemented by provisions to monitor external and internal exposure, including the sampling of workplace air and biological media, such as blood, urine, and exhaled breath, and the specification of analysis methodologies.

EU Directives on safety and health at work must be incorporated into national legislation, but Member States are also entitled to include additional or stricter provisions for the protection of workers. It is therefore important that enterprises check the specific legislation in each relevant country.

In the EU, there are two principal types of OELs, the health-based 'indicative OELs'and the risk-based 'binding OELs' (IOELs and BOELs, respectively).

The respective chemical agents, for which an IOEL can be set, are expected to elicit adverse effects by a threshold mechanism. For such chemical agents, it is possible to identify a threshold concentration, i.e. the exposure level below which exposure to the chemical agent in question is not expected to lead to adverse effects in workers. They are derived from the most recent scientific data available and taking into account the availability of measurement techniques. They are necessary for the determination and assessment of risks by the em-

ployer in accordance with Article 4 of the CAD.
Risk-based BOELs are established for carcinogens, mutagens and airway sensitizers, for which a threshold mechanism is not known.

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3. Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)
4. Regulation (EC) No 1272/2008 of The European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures

INAIL research activity on the assessment of exposure to chemical agents: use of direct reading instruments for dangerous chemicals in the workplaces

Giovanna Tranfo*

Department of Occupational and Environmental Medicine, Epidemiology and Hygiene, National Institute for Insurance against Accidents at Work (INAIL), via Fontana Candida 1, 00078 Monte Porzio Catone, Rome, Italy

*corresponding author: Giovanna Tranfo
Email: *g.tranfo@inail.it*

Key words: occupational exposure; airborne chemicals; gases; sensors; occupational limit values; specificity; exposure profile; exposure peaks.

The Chemical Agents Risk Laboratory of the Department of Medicine, Epidemiology and Environmental and Occupational Hygiene (DiMEILA) of INAIL has the institutional task of carrying out studies, research and monitoring aimed at assessing the conditions of chemical pollution in the workplace and identify appropriate preventive measures; it also develops and standardizes the methods of detection, sampling and analysis of chemical pollutants in working and living environments.

Occupational exposure limits (OELs) existing for chemicals in most cases refer to the usual working shift of 8 hours, as the time weighted mean value of the airborne concentration of the considered chemical should be lower than the limit. This measure is usually performed pumping or letting the air diffuse through a specific absorbing material for about 8 hours; this material is transferred to the laboratory where it is extracted and analyzed by means of sensitive and specific chemical methods like gas-chromatography or liquid chromatography with an appropriate detection device, typically mass spectrometry.

These methods are well known, standardized, and widely used in occupational hygiene.

However, they are quite expensive, time consuming and give no idea of which are the real concentrations to which a worker can be exposed during the work, as the mean value does not give any information about possible exposure peaks, the minimum and the maximum values, in a word, of the exposure profile.

The knowledge of the exposure profile can be very valuable for several reasons, in order to perform a reliable exposure assessment and more in general to protect the workers' health. First, the UNI EN 689 standard on the air sampling in the workplaces requires the knowledge of the exposure profile to establish the sampling time and scheme. Exposure peaks can be due to operations that are out of control, human errors, or other conditions that could be ignored or underestimated if only the mean value is considered.

Some substances have set short term exposure limits (STELs), that is the concentration that workers can be exposed to continuously for a short period of time without risking acute effects, such as throat irritation, that will not be controlled by the application of an 8-hour OEL. These exposure limits are often set for 15 minutes. Some countries have also limited the frequency of peaks to a maximum of 4 peaks/day with a minimal interval of 1 hour. For other substances, peak concentrations should not be exceeded during any time of the workday. Ceiling exposure limits are used for substances, for which short-term peaks of exposure could result in serious health effects – for example, respiratory irritants such as chlorine. For those substances, continuous, direct-reading or short-term instantaneous measurements should be available.

For most carcinogenic substances, an effect threshold cannot be obtained, therefore it is not possible to determine safe exposure levels. Instead of proposing an exposure limit, a quantitative risk assessment may be carried out and admissible exposure levels are established using the concept of so-called acceptable risk. However the knowledge of the real concentrations to which a worker has been exposed should be measured, registered and reduced according to the possibilities given by the technical progress.

All these consideration lead to the need for real time instruments able to measure the concentration of dangerous chemicals in the air of the workplaces in a sensitive, specific and reliable way.

The existing real time instruments are mainly based on the measure of features that are common to chemical classes, like response to UV or IR beams, electrochemical or thermochemical properties; therefore the data are often non-specific, and can be used only for single substances as alarm devices.

In a workplace we usually find many substances at the same time, and the instrument should be able to measure one substance independently from the others, and also be resistant to environmental interference, like dustiness, temperature fluctuations and humidity, electromagnetic interference, falls and vibrations.

For these reasons the research activity has been addressed to the development and validation of new sensor systems, i.e. devices that are in direct interaction with the environment and transform the input amount of target compound into a signal. These systems are based on new technologies for the detection of the pollutant of interest, like the use of nanomaterials and quartz balances, and on new approaches, like the combinatorial selectivity of an array of gas sensors.

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INAIL research activity on the assessment of exposure to biological agents in workplaces

Antonella Mansi*, Emilia Paba, Ilaria Amori,
Anna Maria Marcelloni, Anna Rita Proietto,
Alessandra Chiominto, Paola Tomao

Department of Occupational and Environmental Medicine, Epidemiology and Hygiene, National Institute for Insurance against Accidents at Work (INAIL), via Fontana Candida 1, 00078 Monte Porzio Catone, Rome, Italy

*corresponding author: Antonella Mansi
Email: *a.mansi@inail.it*

Key words: biological risk, occupational exposure limits; bioaerosol, sampling and analytical methods, Volatile Organic Compounds (VOCs), sensors technology.

The Legislative Decree 81/2008 (Title X and X-bis) provides the tools for assessing biological risk and prescribes the measures for the health and safety of exposed workers. The exposure to biological agents (microorganisms, cell cultures and human endoparasites) in working and life environments can cause diseases of infectious, allergic, toxic and carcinogenic nature.
The Biological Agents Risk Laboratory of the Department of Medicine, Epidemiology and Environmental and Occupational Hygiene (DiMEILA) of INAIL carries out research activity aimed to the prevention and control of the exposure risk to biological agents in work and living environments. Briefly, the research activity focuses on i) detection and qualitative-quantitative evaluation of biological agents in environmental matrices and biological samples through innovative methods; ii) identification of markers of exposure to biological agents and assessment of individual susceptibility to airborne allergens; iii) development and standardization of sampling and analysis methods; iv) identification of criteria for assessing exposure to pathogens through epidemiological studies and prevention measures also in scenarios of health emergencies of infectious origin.
Compared to other occupational risks, the biological one is little known and often underestimated due to the lack of Occupational Exposure Limit (OELs)

values that allow the assessment of the risk of exposure to biological agents. However, with regard to some contaminants of biological origin (endotoxin, mycotoxin, allergens and volatile organic compounds) detectable by chemical, immunological or biological assays, validation methods are rapidly going on and some Member States in Europe have set exposure limits for some of these. In recent years, research has made significant progress in the assessment of exposure to bioaerosols in workplaces, but there are still knowledge gaps and technical problems that need to be investigated. For example, there aren't universal sampling techniques, suitable for the great morphological and biochemical variety of airborne biological agents whose presence has been correlated with a wide range of health effects including respiratory diseases (bronchitis, asthma and hypersensitivity pneumonitis), skin problems and gastrointestinal symptoms. Similarly, the currently available microbial detection and identification systems often require long execution times and highly specialized personnel. For this reason, it is needed that the research is increasingly oriented towards the development of rapid, manageable and easy to use analytical methods that allow to overcome the limits of traditional cultivation methods and to provide rapid information for the implementation of appropriate prevention measures. About it, also the European Agency for Health and Safety in the Workplace (EU-OSHA) indicates among the research priorities 2013-2020, the need to develop rapid and innovative methodologies for the detection of biological agents that could represent a risk for occupational health.

In recent years, the procedures for assessing exposure to biological agents have also focused on the detection of indicators of microbiological contamination such as microbial Volatile Organic Compounds (mVOCs), components of the cell membrane, products of primary metabolism and secondary microbial, etc. The use of sensor systems for the detection and identification of chemical substances that can be attribute to specific biological agents would allow the timely identification of any exposure peaks and the monitoring of sources of release of biological agents potentially harmful to health. Through the development of direct measuring techniques for the detection of biological agents in working places will be thus possible to make quick decisions about suitable preventive and protective measures in workplaces.

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Emission of Volatile Organic Compounds from microorganisms and their use for identification

Emilia Paba*, Antonella Mansi, Anna Maria Marcelloni, Ilaria Amori, Anna Rita Proietto, Alessandra Chiominto, Giovanna Tranfo

Department of Occupational and Environmental Medicine, Epidemiology and Hygiene, National Institute for Insurance against Accidents at Work (INAIL), via Fontana Candida 1, 00078 Monte Porzio Catone, Rome, Italy

*corresponding author: Emilia Paba
Email: *e.paba@inail.it*

Key words: Volatile Organic Compounds (VOCs), chemical markers, microorganisms, identification, sensor technology

The growth of microorganisms such as bacteria and fungi generates a broad range of Volatile Organic Compounds (mVOCs) as result of their normal metabolism.

These products typically occur as a complex mixture of low-molecular weight compounds (<300 Da) belonging to different chemical classes including alcohols, alchenes, benzenoids, pyrazines, sulfides, ketones and terpenoids. Their release is influenced by several factors including the growth phase of the microbes, substrate composition, nutrients availability, pH, humidity and temperature [1].

The information from an established database (http://bioinformatics.charite.de /mvoc/index.php?site=home) shows that approximately 2000 organic compounds have been identified as microbial volatiles but it is expected that many more will be identified in the future [2].

The analysis of volatile organic compounds has been proposed as alternative tool to classical microbiological assays for detecting and identifying pathogenic microorganisms. It has been shown that species-specific volatiles may serve as chemical markers for the selective detection of pathogenic species in indoor environments. For example, anisole (methoxybenzene) was identified as a suitable indicator for the detection of *Stachybotrys chartarum*, a toxic mold usually detected in water-damaged building materials [3].

Further to this, these compounds are potenzially detectable before any visible sign of microbial growth, for this reason their use as early indicators of biocontamination has received significant attentions worldwide.

Significant advances in analytical chemical techniques and instruments have facilitated the identification of VOCs with improved sensitivity and accuracy. Gas chromatography–mass spectrometry (GC–MS) is currently considered the gold standard because of its powerful separation capability and highly sensitive detection performance but it is an expensive and time consuming practice that requiers highly qualified personnel. Moreover, GC/MS provides the measure of single compounds, making possible the identification of microrganisms only detecting the presumed compounds species related.

However, the choice of specific compounds is a difficult task due to the great variety of substances produced by microbes and should be based rather on a complex of substances forming a kind of "fingerprints" characteristic for microrganisms, than on individual compounds.

The sensor technology responds well to this requirement since it utilises the differences of compounds' profiles to distinguish among different chemical classes. without the need to separate the mixture into its individual components. The advent of Electronic nose allowed to detect microbial contamination through the changes in odor, especially in clinical diagnosis.

These devices consist of several electronic gas sensors which have sensitivity and selectivity to volatile compounds and respond to the whole set of volatiles producing patterns characteristics in a unique digital pattern attributable to a specific pathogen [4].

The study of these characteristics patterns may allow to detect, discriminate and identify microorganisms also in occupational settings.

Future perspectives should move towards the deepening of the different factors that influence the emission of mVOCs (i.e. the growth substrate composition) and the development of standardised databases containing the VOCs identified for each microorganism found in different environments to be able to identify in real-time the microbial pathogens without the need of culturing them or apply molecular techniques.

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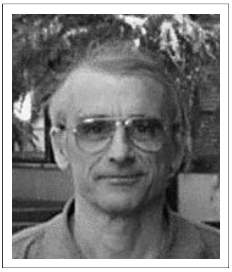
Operating principles of analytical techniques adopted to characterize organic compounds in air



Angelo Cecinato*, Ettore Guerriero, Antonella Macagnano, Massimiliano Frattoni, Mattia Perilli, Catia Balducci

National Research Council of Italy, Institute of Atmospheric Pollution Research (CNR-IIA), Via Salaria km. 29.3, 00015 Monterotondo Stazione RM (Italy)

*corresponding author: Angelo Cecinato
Email: *angelo.cecinato@iia.cnr.it*

Key words: volatile organic compounds (VOCs), air monitoring, environmental analytical chemistry, sensors, online/offline measurements, active/passive sampling.

Nowadays, indoor pollution is among the key topics in environmental sciences, due to impact on safety of life and work places. From both the physical (micro-climatic and fluid-dynamic) and chemical points of view, interiors experience situations very different from outdoors, and also within themselves. In particular, toxicants affecting air show distinct concentration profiles and behaviours, due to extension and nature of surfaces, low level of oxidants like ozone, presence of specific sources, ventilation and air exchange intensity.

The list of chemicals inducing possible threats for humans is very numerous and includes gaseous and particulate substances. Among them, volatile and semi-volatile organic compounds (pure hydrocarbons and oxygen-containing species) are very important and are subject of study because they are capable of inducing short and long term toxicity. Harmful properties of VOCs are not restricted to poisoning and carcinogenicity but include throat, eye and skin irritation, heart and brain problems, infarction, allergies, nuisance of odours; together with semi-volatile and low-volatile organics VOCs impact as mutagenic, endocrine disruptors and promoters of infertility and diabetes (e.g., phthalates, flame retardants and plasticizers).

Due to wide range of concentrations, VOCs are measured by applying specific procedures and instruments. In general, on-line monitoring is performed through dedicated devices (analysers operated in continuous or semi-continuous mode). It allows to know the VOC behaviours at time frequencies better than 1 min but is limited to macro-contaminants (e.g., total and non-methane hydrocarbons); on the other hand, the off-line approach provides information about toxicants occurring at trace and ultra-trace levels. The two approaches are complementary, the former providing an overview of exposure at "normal" working and living conditions, the second picturing extensively events of situations of potential threat for humans and pointing out the sources of risk. An intermediate group of instruments operates in semi-continuous, i.e. accumulates the target toxicant(s) over some fractions of hour and releases their concentrations with the same frequency (e.g., VOC and benzene analysers). In this way a more precise characterization of sites and locations is obtained (e.g., with regard to ozone-precursor hydrocarbons). A recent category of air monitors is represented by sensors, which join quickness and easy access of response, reduced costs and space occupied, non-invasive character, chance of aggregating in rack. Sensors require validation, due to general scarce specificity of their outcomes, however allow to parameterize the indoor air quality through chemical indicators. As for VOCs, devices dedicated to aromatic hydrocarbons (e.g., benzene) and carbonyls (formaldehyde) are available.

When the VOC fraction wants to be characterized, off-line techniques are necessary. The contaminants are enriched from air on traps over a suitable time, then they are extracted and transferred to the analytical instrument for separation, identification and quantitation. Traps or cartridges display manufacturing features depending on target analytes and the purpose of investigation. For instance, when the frequency of sampling is important, VOCs can be collected by means of bags, bottles and canisters (overall for very volatile species) as well as of carbon or polymeric phase cartridges; air is pumped inside, and pressurized or filtered (*active sampling*). When necessary, contaminants are lead to react with derivatizing agents (DNPH in the case of carbonyls). Collection times can last from a handful of seconds up to some hours. Instead, when the average concentration (and cumulated exposure) must be assessed, passive sampling is preferred. Contaminants are accumulated over long periods (days up to months) on the surface of an opportune device, which guarantees constant virtual rate of sampling and preserves from degradation and loss of analytes. It is worth to highlight than the VOC collection devices must be chosen according to molecular range, chemical stability and acid/base properties of analytes; besides, water vapour often interferes and must be eliminated. Figure 1 shows the collection and chemical analysis train usually adopted for volatile hydrocarbons in the case of sampling by means of canisters.

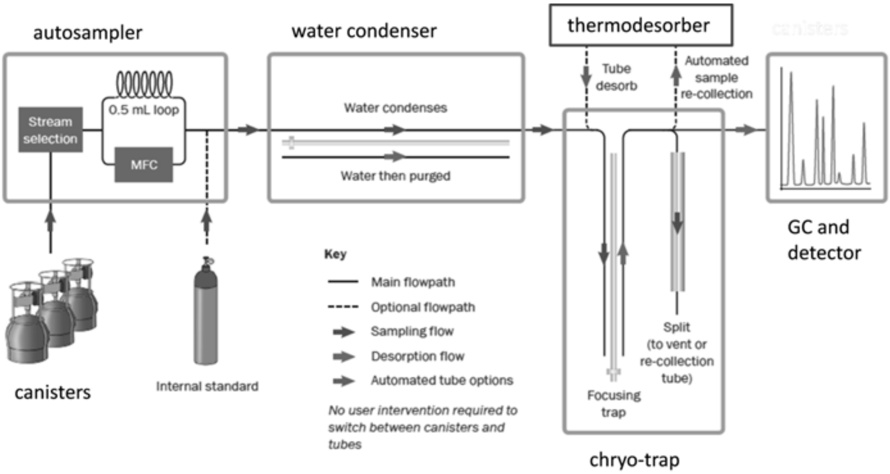


Figure 1: Sampling and analysis apparatus to determine VOCs occurring in air..

The transfer of trapped VOCs from cartridges to analytical apparatus can be attained through following two distinct ways. Compounds can be extracted by eluting with an organic solvent, and an aliquot is sent to analysis; if necessary, operation can be repeated to estimate the overall uncertainty of the measure. Otherwise, the trap can be desorbed by flushing with hot inert gas (helium, nitrogen). In this case, usually the whole air sample is processed during the instrumental analysis, so the quality of measurement is evaluated through parallel samplings. Canisters hypothetically allow one or a handful of individual analyses, depending on the transfer of the entire sample or of fractions to instrument.

Provided that separation of VOCs for identification and quantitation is reached by means of chromatographic columns, analytes are sent to it through a microsyringe and a hot injection port (in the case of solutions) or a hot gas line and a cryogenic trap (in the case of gas mixtures), from which analytes are further thermo-desorbed.

Gas chromatographs are the leading instruments used per VOC analysis. Capillary columns (CC) are able to separate hundreds of compounds in one only run, providing very thin peaks (which multiplies the detector response) and cov-

ering volatility ranges from methane up to highly-boiling substances. Oven temperature gradients reduce the time of analysis.
The characterization of VOCs is provided by various types of detectors, among which the most important are FID, PID and MSD type. Flame ionization is the universal approach to detect VOCs, being non-specific (with a response roughly proportional to C atom amount), linear over a wide range of concentrations, and cheap; on the other hand, it requires ultra-pure and dry hydrogen as auxiliary gas. This is the reason why FID is often replaced by photoionization (PID), which according to UV lamp can limit detection to selected groups of compounds.

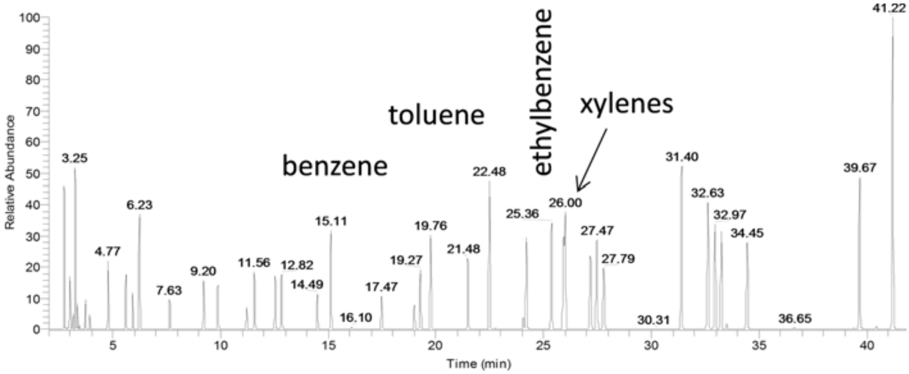


Figure 2: GC-MSD chromatogram of a VOC mixture. C_6-C_8 aromatic compounds are put in evidence.

Mass spectrometry is recently become the most used detection technique when complex mixtures must be analysed, as in the case of atmospheric VOCs. Indeed, it can be universal and contemporarily highly selective, has reached important quality and intensity of signals and approaches the identification of unknown or unexpected compounds.
A special case is represented by volatile carbonyls up to C12. After collection into (DNPH) traps, where aldehydes and ketones react to form the respective hydrazones, the target compounds are eluted by means of acidic acetonitrile and determined through RP-HPLC coupled with UVA. Two distinct wavelengths are usually recorded to resolve acetone and acrolein.

It is worth noting, as conclusion, that organic contaminants cover a very wide range of volatility and most of them at normal conditions coexist in gaseous and condensed phase (as adsorbed on dust and aerosols), Hence, sometimes the determination of both gas and particulate fractions is requested, as in the cases of PCBs, pesticides and dioxins. The approach for monitoring is analogous to that of VOCs, but aerosols and/or dusts must be collected from air or surfaces before extraction and instrumental analysis.

This research was carried out in the framework of a BRIC-INAIL project ID12.

Design and development of a sensor system for the detection of volatile compounds and the identification of micro-organisms in working sites

Corrado Di Natale*

Department of Electronic Engineering, University of Rome Tor Vergata, via del Politecnico 1, 00133 Roma

*corresponding author: Corrado Di Natale
Email: *dinatale@uniroma2.it*

Key words: gas sensors, volatile organic compounds, metabolomics

The air in indoor environments is composed by exogenous and endogenous compounds.

In addition to outdoor sources, a number of volatile compounds have an indoor origin. They are exhaled from furniture, wall tapestries, masonry materials, eventual animals, moulds and fungi. Working places are characterized by additional compounds, often harmful, related to the specific chemical and physical processes. In this context, it is important to control these compounds indoor, to protect the workers, and outdoor, to avoid environmental pollution. It is also important to consider that many compounds, which may be present as traces, may be dangerous either as consequence of acute or long-time exposures. The standard approach to the measure and monitoring of air quality consists in the application of analytical techniques aimed at decomposing the air in its basic components and to determine quantitatively the amount of each element. The high-cost and high complexity of analytical instruments prompts the request for simple to use and low-cost devices. To this regard, modern sensor technologies are expected to fulfil such a requirement.

However, the selective detection of harmful compounds requires the development of specific devices, namely specific chemical receptors. Such a development is not always possible, and on the other hand, it requires large efforts for each compound, and given the large kinds of molecules of interest, it can hardly result in distributed and low-cost devices. Furthermore, selectivity is hardly combined with other fundamental requirements for instance the reversibility necessary for continuous monitoring.

In the last two decades an alternative strategy based on cross reactive sensor arrays has been introduced, based on the simultaneous interaction of multiple molecules with a manifold of sensor elements. This approach mimics the combinatorial principle of olfaction and provides a rapid profiling of complex chemical and biological systems using robust synthetic receptors [1].

In this project the principle of combinatorial selectivity has been applied to the detection of harmful compounds typically linked to working places. The use of cross-reactive sensor arrays also offered the opportunity to detect microorganism through their volatile compounds pattern. Indeed, besides the chemical contamination, working places are sometimes affected by the contamination of moulds and fungi. The detection of microorganisms requires a long laboratory procedure. The analysis of metabolites related volatile compounds (metabolomics) is considered a viable strategy for microorganisms detection and identification and cross-reactive sensor arrays have been demonstrated to be enough sensitive and selective to identify several microorganisms strains [2].

The sensors investigated in this project have been centered on the sensitive properties of porphyrinoids [3]. These are a class of compounds characterized by the necessary versatility for cross-reactive sensor array design. Porphyrinoids based sensors have been prepared using different fabrication methods. The long-established spray coating has been complemented by electrospinning. This last technique made possible the development of innovative hybrid materials where porphyrnoids were mixed with polymers and graphene to give rise to a multifunctional layer that can be used on quartz microbalances and conductometric sensors [4]. Sensors were integrated in a compact and versatile instrument that has been tested in laboratory for the detection of pure compounds and microorganisms and on-field for the identification of microorganisms [5]. Figure 1 shows the designed instrument.

In the same time, to increase the sensitivity of the sensors, in this project the design and test of a temperature controlled purge and trap was also pursued [6]. The development of solid-state sensors is a necessary technological step towards portable and low-cost instruments. However, the properties of analytical instrumentation have always to be kept into consideration. Furthermore, a recent trend in technology is related to the miniaturization of analytical instruments. Thus, for this reason in this project also the properties of FTIR spectroscopy has been investigated for the detection of specific compounds in well selected applications [7].

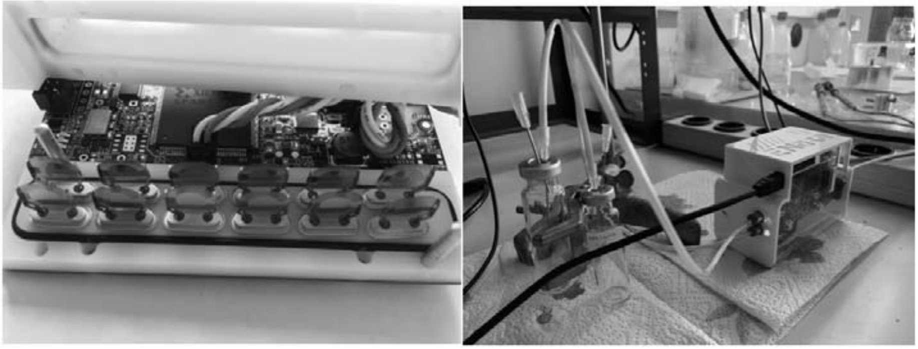


Figure 1: left: detail of the array of 12 QMB sensors. Right: The QMB based instrument during the tests of exposure to VOCs.

Finally, this project offered the opportunity for a wide range approach to the monitoring of volatile compounds in working places. Innovative sensors and instruments have been developed that demonstrated their potentiality in monitoring volatile compounds of different origin, included those marking the presence of contamination of microorganisms.

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Heterogeneous nanofibrous polymer layers to get ultra-sensitive and tunable conductive sensors for indoor monitoring

J. Avossa[1], E. Zampetti[1], R. Paolesse1,3, C. Di Natale[1,4], F. De Cesare[1,2], A. Bearzotti[1], A. Capocecera[1], P. Papa[1], G. Scarascia-Mugnozza[2], E. Zussman[5], G. Tranfo[6], A. Macagnano*[1,2]

[1]*Institute of Atmospheric Pollution Research (IIA), National Research Council (CNR), Monterotondo (RM), Italy;*
[2]*Department of Innovation in Biological Systems, Agro-Food and Forestry (DIBAF), University of Tuscia, Viterbo, Italy;*
[3]*Department of Chemical Science and Technologies, University of Tor Vergata, Rome, Italy;*
[4]*Department of Electronic Engineering, University of Tor Vergata, Rome, Italy;*
[5]*Department of Mechanical Engineering, Technion, Haifa, Israel*
[6]*DIMEILA-INAIL, Monteporzio Catone (RM), Italy*

*corresponding author: Antonella Macagnano
Email: *antonella.macagnano@cnr.it*

Keywords: nanofibrous sensing materials, conductive microelectrodes, gas and VOCs detection, H2TPP, mesoporous graphene

Introduction – The inaccurate quantification of personnel exposure to indoor air pollution introduces error in health estimations, severely limiting causal implication in epidemiological research worldwide. Rapid advancements in sensor technologies have offered the potentials to overcome this limitation. Currently, electrospinning is considered as one of the most versatile and inexpensive manufacturing technologies to design and develop nanostructured sensors to detect effectively gases and volatile organic compounds (VOCs) in the air [1]. Sensors based on polymeric fibers look extremely attractive for their features, like ease of preparation, low cost and great versatility, high selectivity and sensitivity. The attention has been focused on the challenging goal of obtaining conductive sensors employing suitable scaffolds of eco-friendly (polyhydroxybutyrate) and sustainable (recycled) nanomaterials (polystyrene) [2]. Indeed biodegradability is a noteworthy feature to obtain sensing tools environmentally friendly and safe for health. However, sensors for gas monitoring must also be able to both persist intact for a useful shelf life and to preserve their sensing features over time, depending on the specific application and the working period. The conductivity of the planned sensors has been implemented by adding conductive nanoparticles (e.g. mesoporous graphene's flakes). The selectivity has been tuned by introducing a functionalized macromolecule sensitive to several classes of gas and VOCs. Therefore, H_2-tetraphenylporphyrin (H_2TPP) [3], that resembles naturally occurring porphyrins, has been synthesized and solubilized within the selected polymer blends suspensions and subjected to electrospun deposition on interdigitated metal electrodes. The novel sensors resulted tuneable in sensing several gases and VOCs by both changing the amount of graphene inside fibers and adding H_2TPP. Additionally, changes in the working temperature within a range of 25°C and 60°C, achieved promising sensing features potentially useful for indoor pollution monitoring.

Experimental - Chemicals were all purchased from Sigma-Aldrich. H_2TPP was synthesized according to the Adler's method. Electrospinning depositions were carried out in a home-made apparatus (DC Voltage: 3-6 kV, distance: 5 cm). Sensors (7 x 11 mm) were sealed in a measurement chamber (250 ml) and exposed to known concentration of vapours and gas.

Results and Discussion - The electrodes were successfully coated with thin layers made of PS/PHB/MGC and PS/PHB/MGC/H_2TPP non-woven fabrics, respectively, whereas each sensor resulted different in morphology and sensing performances (Fig.1). The immiscibility of the two polymers (PS and PHB) allowed the production of rough fibers [3]. The addition of porphyrins tuned both colour, roughness and conductivity. Therefore, fibers hosting H_2TPP was thinner and smoother than PS/PHB/MGC ones and with ellipsoidal growths. Sensor conductivity, depending on MGC amount and distribution (0.93% mass ratio), augmented with temperature increasing and when porphyrins were hosted inside fibers. Temperature affected also responses to the VOCs both in kinetics and sensitivity values. Several gases (NO_2, NH_3, H_2S) and chemical compounds (ketones, aromatic hydrocarbons, organic acids) were tested as potential analytes. Apparently, porphyrins favoured VOCs interactions when the sensor temperature increased. The metal-core and temperature strongly affected the sensors selectivity.

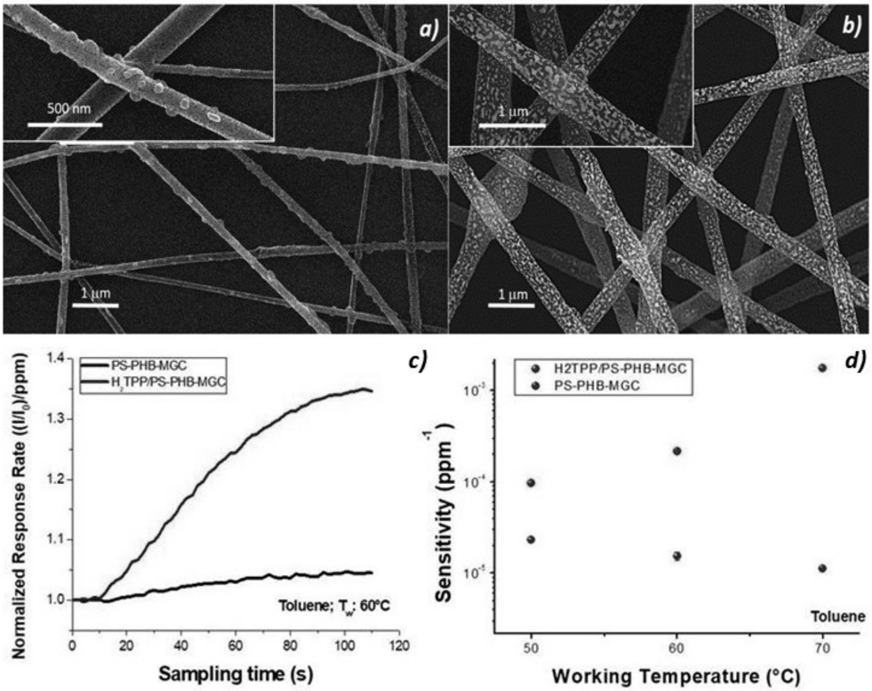

Fig.1. SEM pictures of the polymer fibers with the porphyrin *(a)* and without *(b)*. Comparison of the normalized response rate *(c)* and sensitivities *(d)* of both H_2TPP-PS-PHB-MGC and PS-PHB-MGC sensors to toluene.

Conclusions - Rapid responses and good analyte selectivity were reported. Porphyrins were supposed to be the responsible of a better distribution of MGC along fibers giving to the fibers homogeneity in size and morphology, resulting also in the sensor current increasing. Chemosensor without porphyrins showed a huge selectivity for NO_2, H_2TPP increased selectively the sensor sensitivity to some VOCs, overall at higher temperature values (and especially for toluene at 60°C). The use of polymers obtainable from recycled (PS) and biodegradable plastics (PHB) as a sensor framework sounds to be a promising strategy for the development of smart and more eco-friendly scaffolding for chemical sensors.

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FTIR spectroscopy as a tool for a quantitative evaluation of volatile organic compounds (VOCs) in air

Giancarlo Della Ventura*[1,2], Francesco Radica[1],
Plinio Innocenzi[3], Luca Malfatti[3], Augusto Marcelli[2,4]

[1]Department of Science, University of Roma Tre, Largo S. Leonardo Murialdo 1, 00146 Rome (Italy)
[2]INFN Laboratori Nazionali di Frascati, Via E. Fermi 40, 00044 Frascati, Italy
[3]Laboratorio di Scienze dei Materiali e Nanotecnologie, CR-INSTM, Via Vienna 2, Sassari, Italy
[4]RICMASS, Via dei Sabelli 119A, 00185 Rome, Italy

*corresponding author: Giancarlo Della Ventura
Email: *giancarlo.dellaventura@uniroma3.it*

Key words: volatile organic compounds, occupational exposure, sensors, FTIR spectroscopy

Styrene is a colourless substance that evaporates easily. In its pure form, styrene has a sweet smell; manufactured styrene may contain aldehydes, which give it a sharp, unpleasant odour. Large amounts of styrene are produced in industry (> 20.000 tons/year globally) to make plastic and rubber, but small amounts are also produced naturally by plants, bacteria, and fungi. Consumer products containing styrene include packaging materials, fiberglass, plastic pipes, automobile parts, drinking cups and other "food-use" items. In most of these products styrene mainly occurs linked together in long chains (polystyrene). A large number of workers are potentially exposed to styrene. The highest potential exposure occurs in the reinforced-plastics industry, where workers may be exposed to high air concentrations and also have dermal exposure to liquid styrene or resins. The most common health problems in people exposed to styrene involve the nervous system, including changes in colour vision, tiredness, feeling drunk, slowed reaction time, concentration problems, and balance problems. The International Agency for Research on Cancer of WHO included this substance in the list of possible carcirogen factos, in the group 2B (e.g. IARC Monograph, 2002[1]). Different Occupational Exposure Limits (OELs) have been set by EU members; in Italy these are 20 ppm as 8-hours Time-Weighted-Average (TWA) and 40 ppm as Short-Term-Exposure-Limit (STEL, 15 min). There are a number of different analytical test equipment for styrene on the market; the most simple provide spot visualization of the exposure level, such as glass-tubes with discolouring media, other provide 8-hrs averages, such as active carbon badges. Portable monitoring equipment are typically based on Photo-Ionization-Detection (PID) systems, and these provide fast response and possibility to store data. These systems however do not allow discrimination of different volatile phases. For this purpose, Infra-Red (IR) analysis or gas chromatography (GC) need to be be used. These latter techniques are however not suitable for real time monitoring, are expensive and require skilled operators. In this work we developed improved methods exploiting Medium-Infra-Red (MIR) spectroscopy for the real-time monitoring of styrene[2], eventually occurring with other VOCs in the atmosphere, down to a detection limit better that 1 ppm. Several VOCs were tested; the procedure was initially set-up by using a laboratory FTIR spectrometer, equipped with a Globar source and a DTGS detector. Increasing controlled amounts of liquid VOC were introduced into the measuring chamber and let evaporate completely; the concentration of the gas was measured simultaneously with a PID and by FTIR allowing calibration curves to be determined for all VOC species.

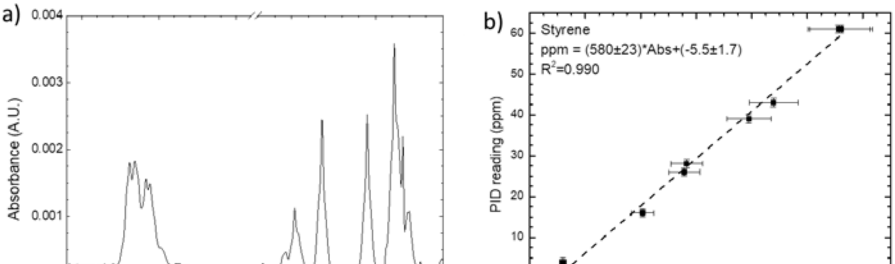

Fig. 1: (a) Typical styrene FTIR spectrum in the MID range; (b) the PID reading (ppm) against the integrated absorbance of the styrene absorbance of at 910 cm^{-1}.

Figure 1a shows a selected spectrum measured for styrene in the MID-IR, where the characteristic peaks are highlighted, while Figure 1b shows the excellent agreement between the amount of styrene measured by the PID system and the integrated absorbance of one selected peak in the spectrum at 910 cm^{-1}. Similar correlations are observed for other peaks in the spectrum, as well as for different VOCs, suggesting that the amount of the single volatile phase can be discriminated in the spectrum of a multiphase gas mixture, providing there is no significant overlap for the selected bands. Based on the calibration curves established for the single VOCs we performed several blind tests analysing mixtures of unknown relative amounts of styrene plus a second unknown component. The FTIR spectra provided a fast identification of this component (acetone) and yielded relative amounts in the mixture very close to the actual values. Once set-up with additional experiments, the technique was tested by means of a portable FTIR Bruker Alpha II FTIR spectrometer, used as an intermediate step toward the design of a compact instrument to be eventually coupled to sensors based on porphyrinoids for an integrated monitoring system (this volume). The design of the experimental lay out is shown in Figure 2.

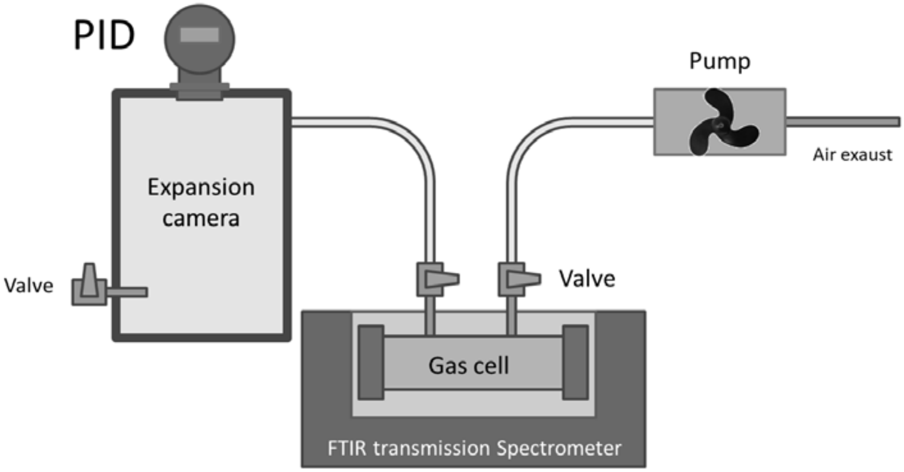

Fig. 2: The experimental set-up used for the compact low volume FTIR system: the liquid VOC is introduced inside the expansion camera and the resulting concentration in air is measured via a PID; at equilibrium the gas is transferred to a pre-evacuated gas cell within the FTIR spectrometer and measured in the MIR range.

A typical spectrum of ethanol is given in Figure 3a, while Figure 3b shows a calibration curve obtained for this volatile phase. Inspection of Figure 3b shows that there is an excellent linear relationship between the PID derived gas concentration within the cell and the measured IR absorbance, demonstrating the reliability of the technique at low gas concentrations.

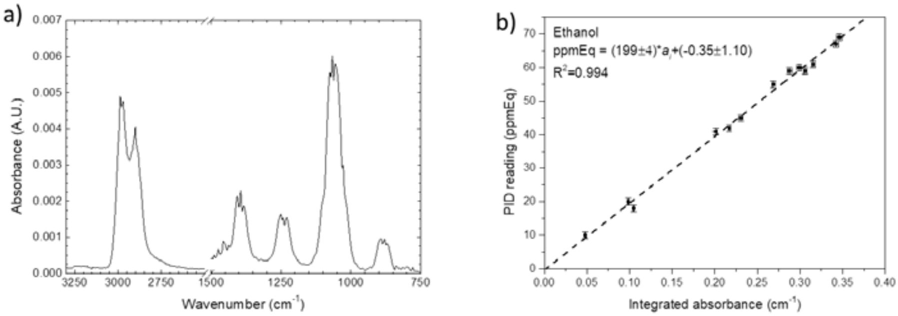

Fig. 3: (a) FTIR spectrum of ethanol collected at 4 ppm concentration in the chamber as determined *via* the PID detector; (b) calibration curve obtained by integrating ethanol 1066 cm^{-1} absorption peak.

This research was carried out in the framework of a BRIC-INAIL project ID12.

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In vitro identification of *Aspergillus* species and indoor air analysis using a QMB-based gas sensor array

Rosamaria Capuano*[1], Antonella Mansi[2], Emilia Paba[2], Andrea Gordiani[2], Nunziata L'Episcopo[2], Anna Maria Marcelloni[2], Alessandra Chiominto[2], Anna Rita Proietto[2], Emiliano Zampetti[3], Antonella Macagnano[3], Alexandro Catini[1], Roberto Paolesse[4], Giovanna Tranfo[2], Corrado Di Natale[1]

[1]Dipartimento Ingegneria Elettronica, Università di Roma Tor Vergata, Roma; Italy
[2]INAIL, Monteporzio Catone (Roma), Italy
[3]CNR-IIA, Monterotondo (Roma), Italy
[4]Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Roma; Italy

*corresponding author: Rosamaria Capuano
Email: *capuano@ing.uniroma2.it*

Key words: gas sensor array, indoor air quality, microorganisms, Volatile Organic Compounds (VOCs)

The identification of microorganisms through the analysis of their volatile metabolites is suggested as a viable alternative to long and costly microbiology procedures [1].

It is indeed known that microorganisms produces a wide range of volatile organic compounds (VOCs) including, among the others, also aldehydes, esters and sulfides.

Analytical chemistry offers a number of instruments, from gas chromatography to the various declination of mass spectrometers, that have been fruitfully used for the identification of bacteria from their volatile metabolites [2]. However, this instrumentation, although very accurate, is costly, bulky and it needs trained operators.

Cross-reactive sensor arrays (also known as electronic noses) have emerged as a strategy to rapidly profile complex chemical and biological systems. Array-based sensors generate patterns of signal from the sample that are subsequently classified by pattern recognition algorithms to identify different sources of volatile compounds. The capability of this approach to identify bacteria has been recently shown [3].

In the BRIC16-ID 12/2016 project a gas sensor array has been developed and its application to the identification of microorganisms is here presented. The sensor array is made of 12 quartz microbalances (QMB) each coated with a diversely sensitive and cross-reactive material. Eight sensors were coated with spray casting films of different porphyrinoids [4] and four were functionalized by electrospin mixtures of polymers, porphyrins and graphene. [5]

The sensor array was tested in two different experiments. In the first, the VOCs released by cultures of *Aspergillus niger, Aspergillus flavus, Aspergillus fumigatus* were measured. The microorganisms were inoculated onto Potato Dextrose Agar (PDA) kept in Petri dishes and measured different times of growth. Fig. 1 shows the scores plot of the principal component analysis of the sensors data. The best separation between micro-organisms is obtained at third day from inoculation.

On-field tests were performed in some indoor environments where a fungal contamination has been detected. The data were again analysed by principal component analysis and the resulting scores plot is shown in figure 2. Results demonstrate that microbiological contaminated environments can be clearly discriminated from contamination-free environments. GC-MS results shows the presence of some VOCs but further studies are needed to understand if there is a relation between these compounds and the fungal species found in contaminated environments.

These results demonstrate that the sensor developed in this project has the potentialities to be routinely applied for the indoor control of biological contamination caused by fungal species belonging to *Aspergillus* genus.

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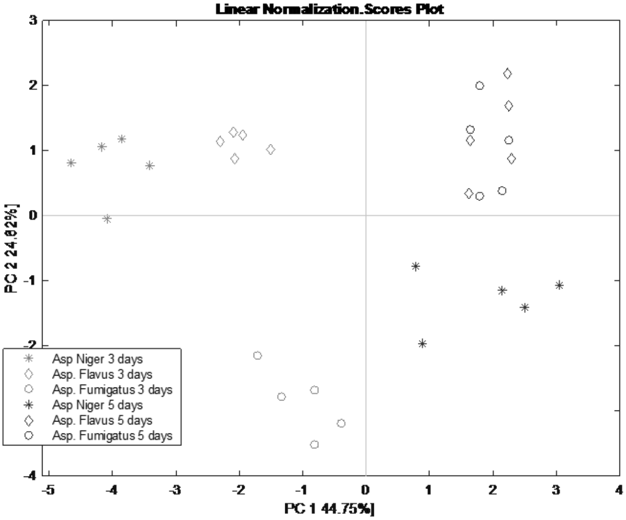


Fig. 1: Scores plot of the first two principal components of the electronic nose data.

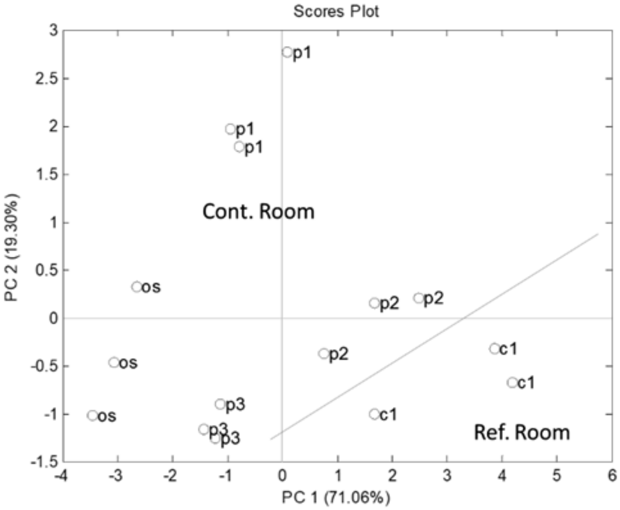
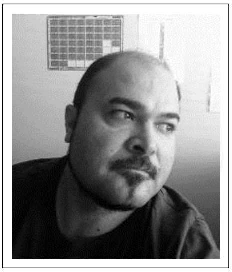


Fig. 2: Scores plot of the first two principal components of the electronic nose data. Label: wall 1 of contaminated room (p1); wall 2 of contaminated room (p2); open space of contaminated room (os); wall 3 (p3), open space control room (c1).

Design of a portable VOCs measurement system based on a thermal controlled trap



E. Zampetti*[1], A. Macagnano[1], P. Papa[1], A. Capocecera[1], J. Avossa[1], A. Bearzotti[1], A. Cecinato[1], C. Balducci[1], R. Capuano[2], C. Di Natale[2], G. Tranfo[3]

[1]Institute of Atmospheric Pollution Research (IIA), National Research Council (CNR), Monterotondo (RM), Italy;
[2]Department of Electronic Engineering, University of Tor Vergata, Rome, Italy;
[3]Department of Occupational and Environmental Medicine, Epidemiology and Hygiene, National Institute for Insurance against Accidents at Work (INAIL), via Fontana Candida 1, 00078 Monte Porzio Catone, Rome, Italy

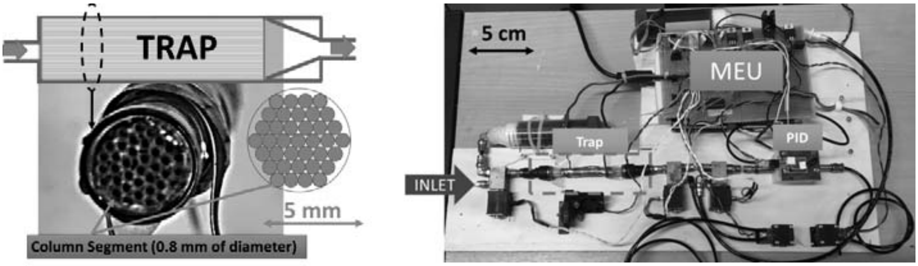
*corresponding author: Emiliano Zampetti
Email: *e.zampetti@iia.cnr.it*

Keywords: VOCs separation, portable VOCs measurement system, BTEX.

Introduction – In this paper we present the design and development of a portable instrument for measuring VOCs in air. The intent was to study a method to provide a separation of the different compounds in the sampled air (VOCs polluted). The core of the system is a trap made up of several segments of a chromatographic column arranged into a suitable form factor. By employing a temperature controller, a pneumatic system and a main control unit (MEU), it is possible to use the system in two different ways: i) Mode A (adsorption and thermal desorption) where the trap samples and retains the VOCs to be analyzed. Using different trapping temperatures, the device is able to desorb in a selective manner the compounds going to the detector; ii) Mode B (real time measurement and thermal controlled chromatographic separation), where, the trap temperature can be set to different values during the sampling and measuring. In this way, the trap absorbs VOCs and releases them at different times (like to a chromatographic column).

Experimental – Figure (a) shows a sketch and a picture (front view) of the developed trap. The trap consists of 35 segments of ZB-624 chromatographic column (phase: 3 µm thick of 6% Cyanopropylphenyl 94% Dimethylpolysiloxane, used for VOCs and Residual Solvents) arranged into a suitable composition (80 mm long and 0.8 mm of diameter). MEU controls the overall system functioning, such as the sampling, the trap temperature, the desorbing process and the fluid-dynamic delivering system (Figure b). Finally, a photo ionization detector (PID by IONSCIENCE) is used at the end of the measurement chain to measure the VOCs' concentrations. A purpose-made software records the real time data and sets the overall parameters.

Results and Discussion – The system was tested both in A and B mode with compounds such as: benzene, toluene, p-xylene, styrene, ethanol, acetone. In mode A we have obtained good results in terms of selective thermal desorption of benzene from toluene and xylene, with concentrations in the order of tens to hundreds ppm. In mode B we have obtained an effective temporal separation for benzene, toluene, xylene and styrene from the other interfering VOCs, measuring, in real time, concentration in the order of tens ppb up to a few ppm.



a) b)

Fig.1: Trap prototype (a) it is based on 35 chromatographic column segments 80 mm long with an inner diameter of 0.8 mm. System prototype (b) it is a portable system able to measure VOCs in the range of 0.01 to 3000 ppb.

Conclusions – We have designed and tested a portable system to measure VOCs in particular BTEX. We have developed a trap, the core of the proposed system, that can be used in two ways: Mode A (adsorption and thermal desorption), Mode B (real time measurement and thermal controlled chromatographic separation). This system could be used standalone or integrated to a chemical sensor array, such as an E-Nose, devoted to measure complex matrices of chemicals.

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THz spectroscopic characterization of liquid-phase VOCs

Annalisa D'Arco*[1], Marta Di Fabrizio[2], Valerio Dolci[3], Augusto Marcelli[4,5], Massimo Petrarca[3], Giancarlo Della Ventura[4,6] and Stefano Lupi[2,4]

[1]*INFN – Section of Rome 'La Sapienza', P.le Aldo Moro 2, 00185 Rome, Italy*
[2]*Physics Department, University of Rome 'La Sapienza', P.le Aldo Moro 5, 00185 Rome, Italy*
[3]*INFN and SBAI, Department of Basic and Applied Sciences for Engineering, University of Rome 'La Sapienza', Via Scarpa 16, 00161 Rome, Italy*
[4]*INFN-LNF, Via E. Fermi 40, 00044 Frascati, Italy*
[5]*Rome International Centre for Material Science Superstripes - RICMASS, Via dei Sabelli 119A, 00185 Rome, Italy*
[6]*Science Department, University of Roma Tre, Largo S. L. Murialdo 1, 00146 Rome, Italy*

*corresponding author: Annalisa D'Arco
Email: *annalisa.darco@roma1.infn.it*

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Volatile organic compounds (VOCs) are diverse and reactive chemicals, characterized by different functional groups, including various aromatic chloro hydrocarbons and perfluorocarbons, such as organic solvent thinners, degreasers, cleaners, lubricants, inflammable liquids [1-4]. Chemical and petrochemical industries and activities, building products and furnishing materials, vehicle exhausts, fuel combustion and evaporation, solvent usage are the major anthropogenic sources of VOCs [1-4]. Thus, in the fields of Occupational Safety and Health and Environmental Protection, VOCs deserve special considerations as a potential source of risk for humans and environment [5-8]. As VOCs are increasingly recognized as pollutants [2,3], thus a fast, non-destructive, and useful tool for the detection of and chemical identification is highly desirable, with a focus on low-cost, low-power consumption and low-time consuming devices. New and advanced technologies, such as Terahertz (THz) spectroscopies, may provide complementary methods to conventional analytical approaches

[9-12]. In particular, THz time-domain spectroscopy (THz-TDS) has become a promising candidate for characterization of samples in a wide range of research fields, such as biology, medicine, environmental investigations, material science and security. This spectroscopic technique has many advantages over the traditional ones, it is insensitive to the thermal background and thus has a higher signal-to-noise ratio (SNR); and it is extremely sensitive to the conformation and structure of molecules.

This work addresses the application of THz-TDS by investigating some different VOCs in liquid phase belonging to alcohols and aromatic hydrocarbons categories: acetone and methanol for alcohols category, and benzene, styrene, toluene, and p-xylene for the second one.

The chemical structures of VOCs, here investigated for each category, are characterized by the same chemical formulas, modified by different C-H_X functional groups, which are expected to induce changes in their optical properties.

Their THz spectra have been measured in liquid phase at room temperature, using THz-TDS home-made system. Their frequency-dependent refractive index and absorption coefficient have been extracted and analyzed in the spectral range from 0.2 to 2.5 THz. In figure 1, we report the measured optical properties for aromatic hydrocarbons. The optical properties of bi-component VOCs mixtures have also been investigated, and described in terms of a linear combination of pure VOCs optical components.

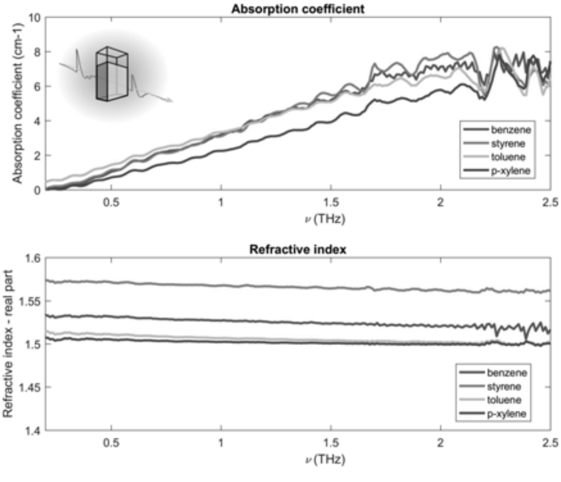

Fig. 1: Absorption coefficients and refractive indexes of benzene, styrene, toluene and p-xylene vs. frequency.

Although the samples shown have similar molecular structures, the measurements of the refractive index and the absorption coefficient in the THz region (0.2-2.5 THz) revealed that specific VOCs can be efficiently discriminated, demonstrating the sensitivity of the THz spectroscopy method as alternative detection tool for VOC pollutants in their liquid phase.

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Shedding light on molecules of environmental interest with novel XUV sources

Marcello Coreno*[1,2], Lorenzo Avaldi[1], Carlo Callegari[1,2], Stefano Orlando[1], Susanna Piccirillo[1,3]

[1]1SM- CNR, Basovizza AREA Science Park, 34149 Trieste, Italy.
[2]Elettra Sincrotrone Trieste, ss. 14, km. 163,5 34149 Basovizza Trieste, Italy.
[3]Dip. Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata", Via della Ricerca Scientifica, 00133 Rome, Italy

*corresponding author: Marcello Coreno
Email: *marcello.coreno@cnr.it*

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How do aerosol particles form in atmospheres? How do differences in chemical bonding mechanisms affect molecular reactivity? How do they affect molecular photochemistry in dense and rarefied media? To significantly advance our understanding of such outstanding questions CNR and Elettra Sincrotrone Trieste have been developing a synchrotron radiation based chemical-physics laboratory at the Gas Phase beamline (Elettra, Trieste, I). The answer to these, and to analogous fundamental and applied questions rely in fact also on a detailed understanding of the electronic and structural dynamics of isolated molecules interacting with radiation such as photons of different wavelength.

For the last two decades the GasPhase[1, 2] beamline has enabled thorough studies of the energetics and chemical reactivity of different class of molecules, including those of biological and environmental interest by means of photoionization techniques and different types of mass spectrometry. The flux of the beamline and the efficiency of the experimental end-stations has allowed to tackle even low-density targets such as molecular vapours[3] or nanoaggregates[4].

More recently the interest of the physical chemistry-chemical physics community has been captured by the opportunity of exploring the temporal dynamics in chemical processes by means of novel XUV light sources. For this reason, two new beamlines capable of delivering ultrafast EUV photon pulses have recently been commissioned in the framework of the FERMI Free Electron Laser (FEL) project: the Low Density Matter beamline at FERMI [5, 6] and CITIUS [7, 8], a state-of-the-art fs-VUV source, based on laser High Harmonic Generation on rare gases.

Finally, the project of the new beamline MOST (namely "*MOlecular Science and Technology*") for Elettra2.0, the new facility being built in Trieste, will also be outlined. The project will build on the well-established experience of the GasPhase and Circular Polarization beamlines and the expertise of their user communities in the study of fundamental processes on organic and biomolecules, radicals, clusters, dimers and droplets as well as in the investigation of dynamic processes on ps scale via pump probe experiments and dichroic studies of molecules of increasing complexity.

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